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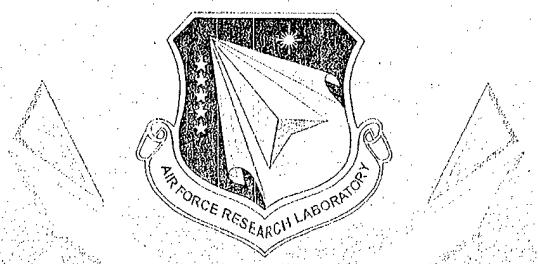

The Specific Refractive Index Increments for POSS Polymers in Solution.

Sherly R. Largo[₸], Timothy Haddad[₸], Constance Schlaefer[¥] and Rene Gonzalez[¥]

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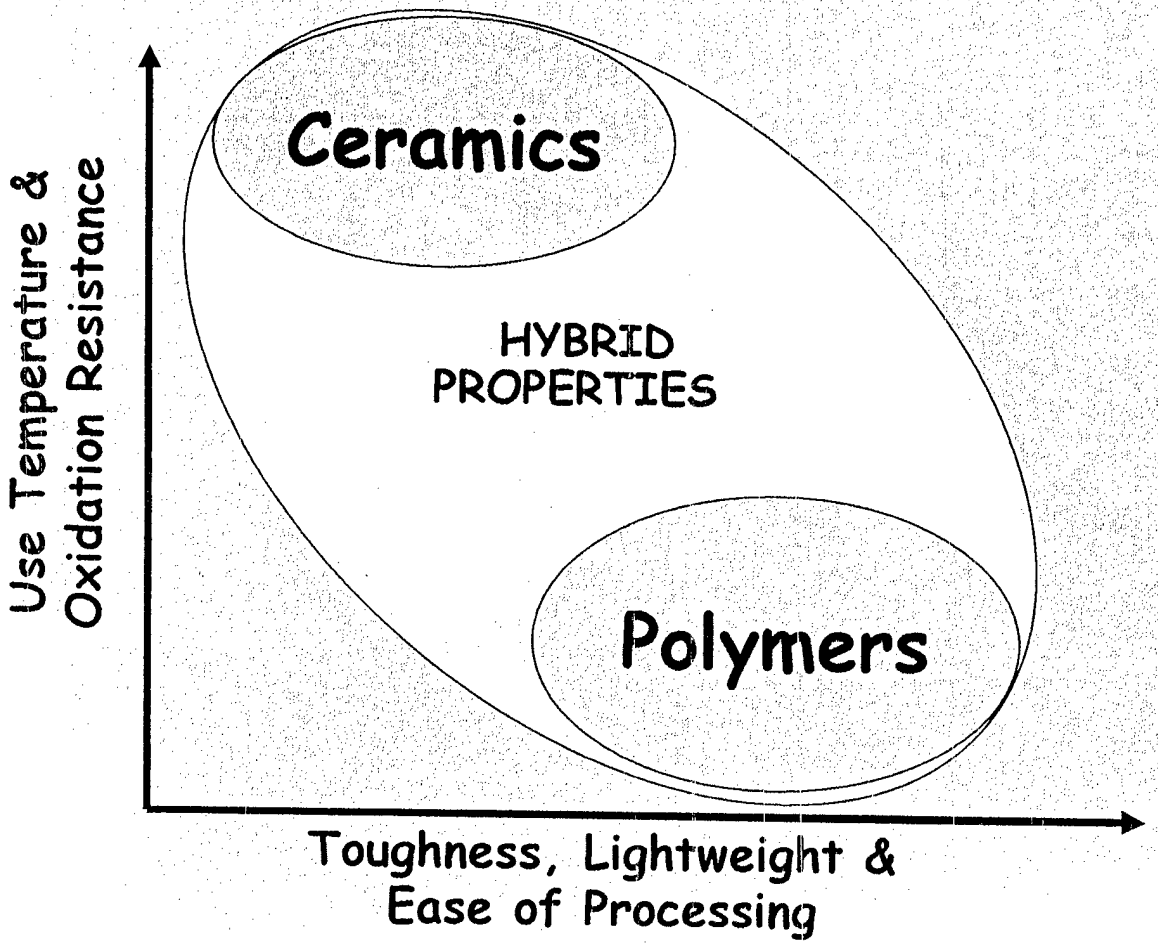
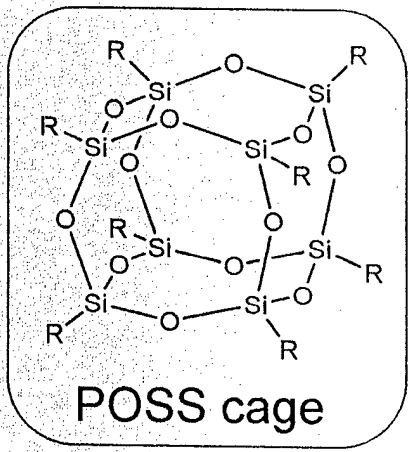
Hybrid Inorganic/Organic Polymers

Goal: Develop High Performance Polymers that REDEFINE material properties

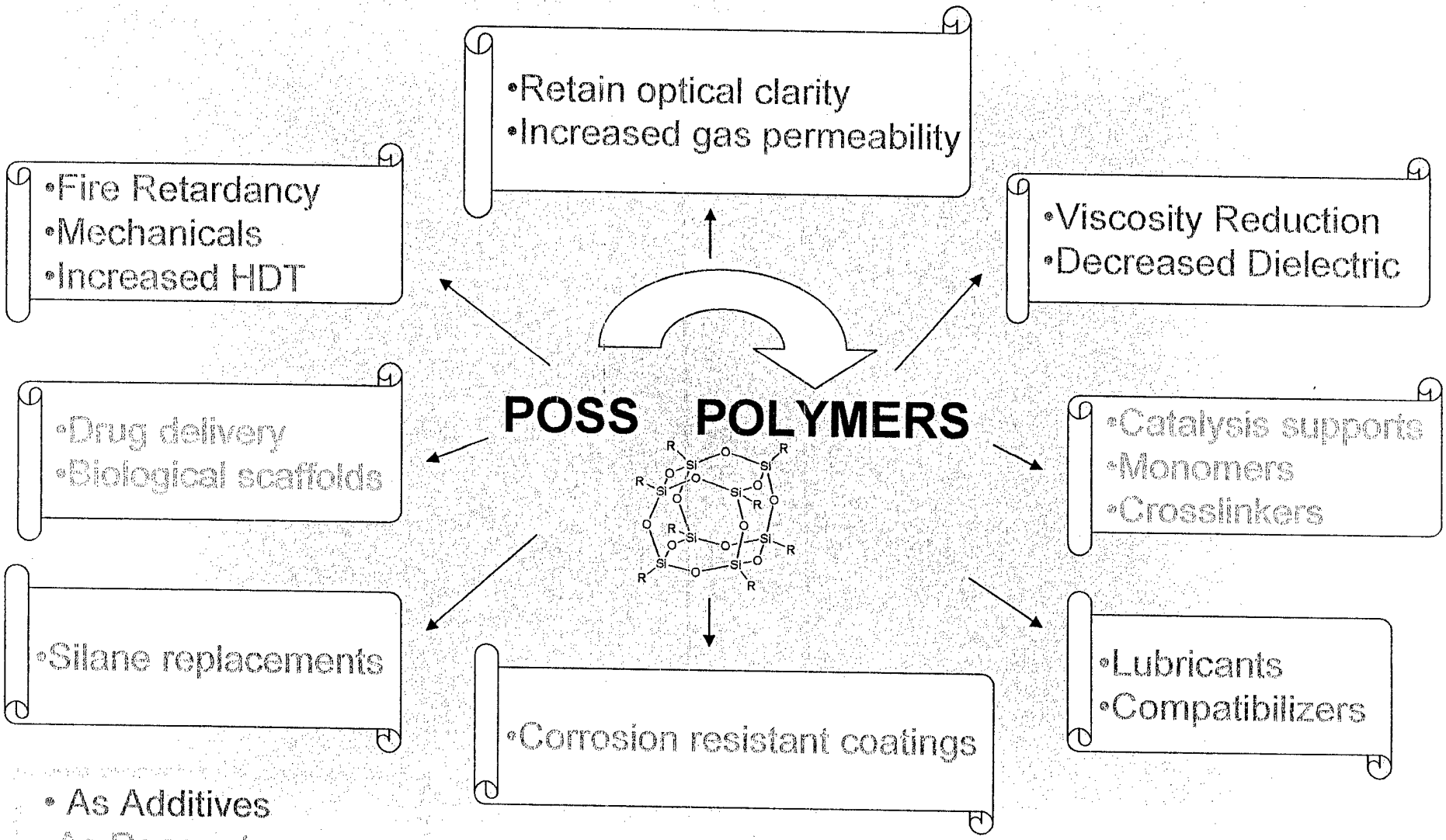
POSS – Polyhedral Oligomeric SilSesquioxanes



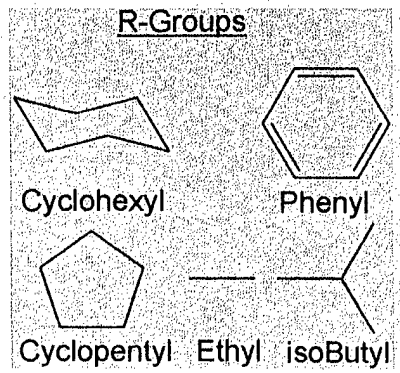


•Hybrid Plastics bridge the differences between ceramics and polymers

Introduction to POSS

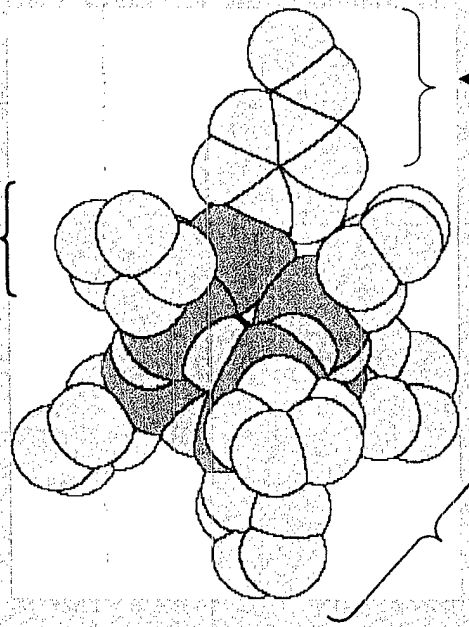


Anatomy of a POSS Nanostructure



Nonreactive organic (R) groups for solubilization and compatibilization.

Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

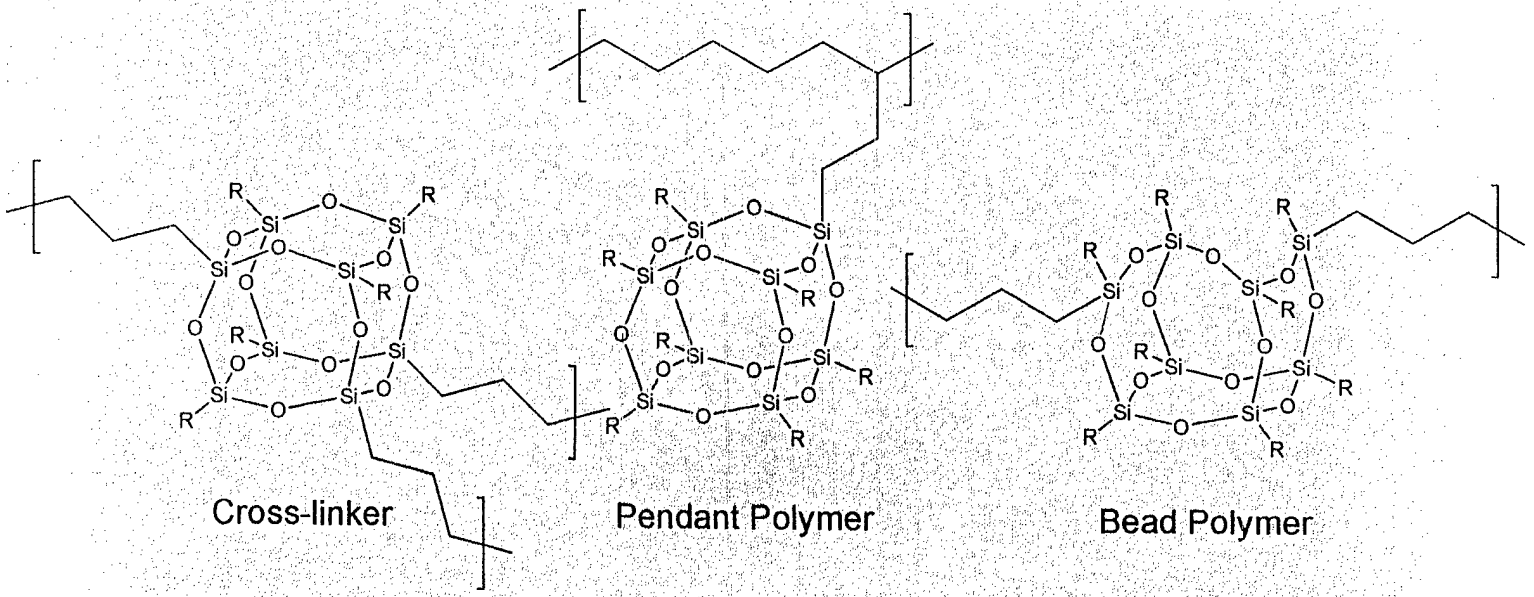


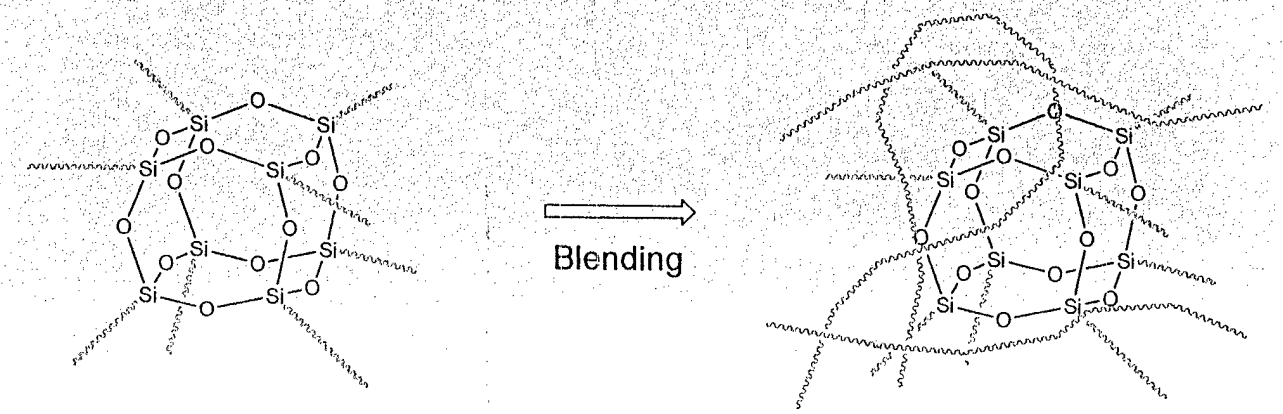
May possess one or more Functional groups suitable for Polymerization or grafting.

Thermally and chemically robust hybrid (organic-inorganic) framework.

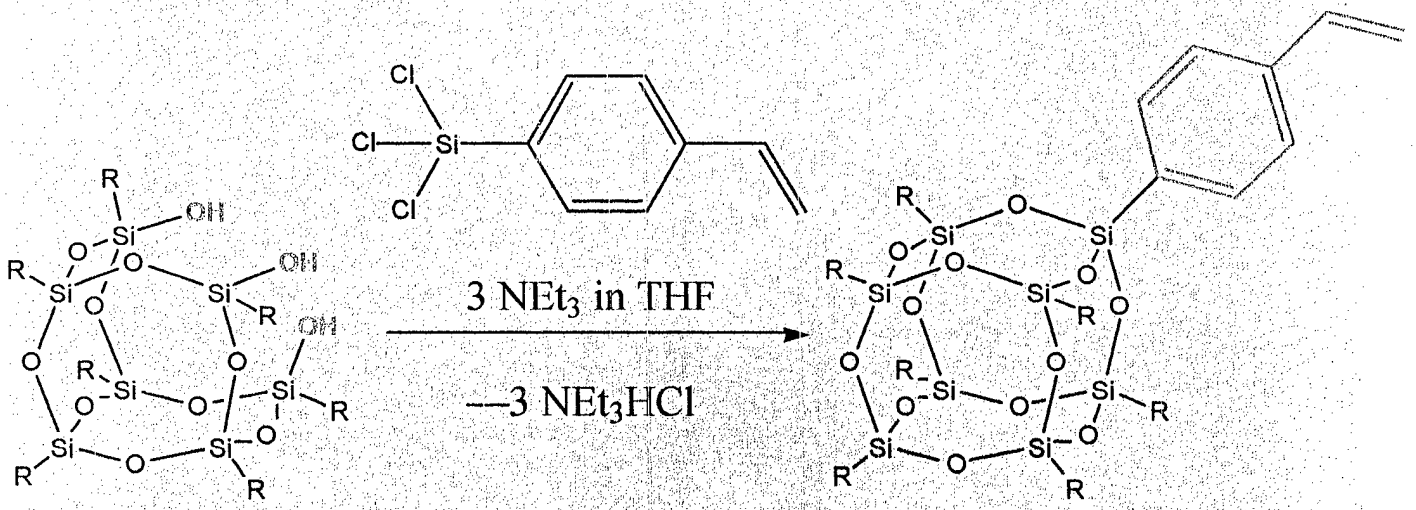
Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

POSS Polymer Incorporation



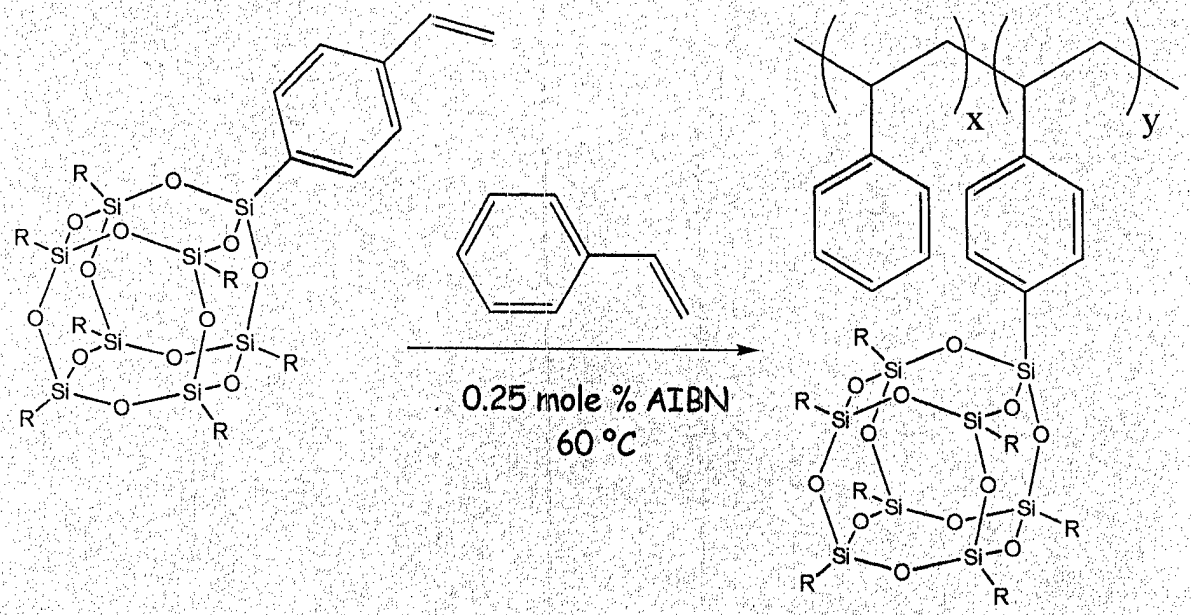


POSS Styrene Monomer Synthesis



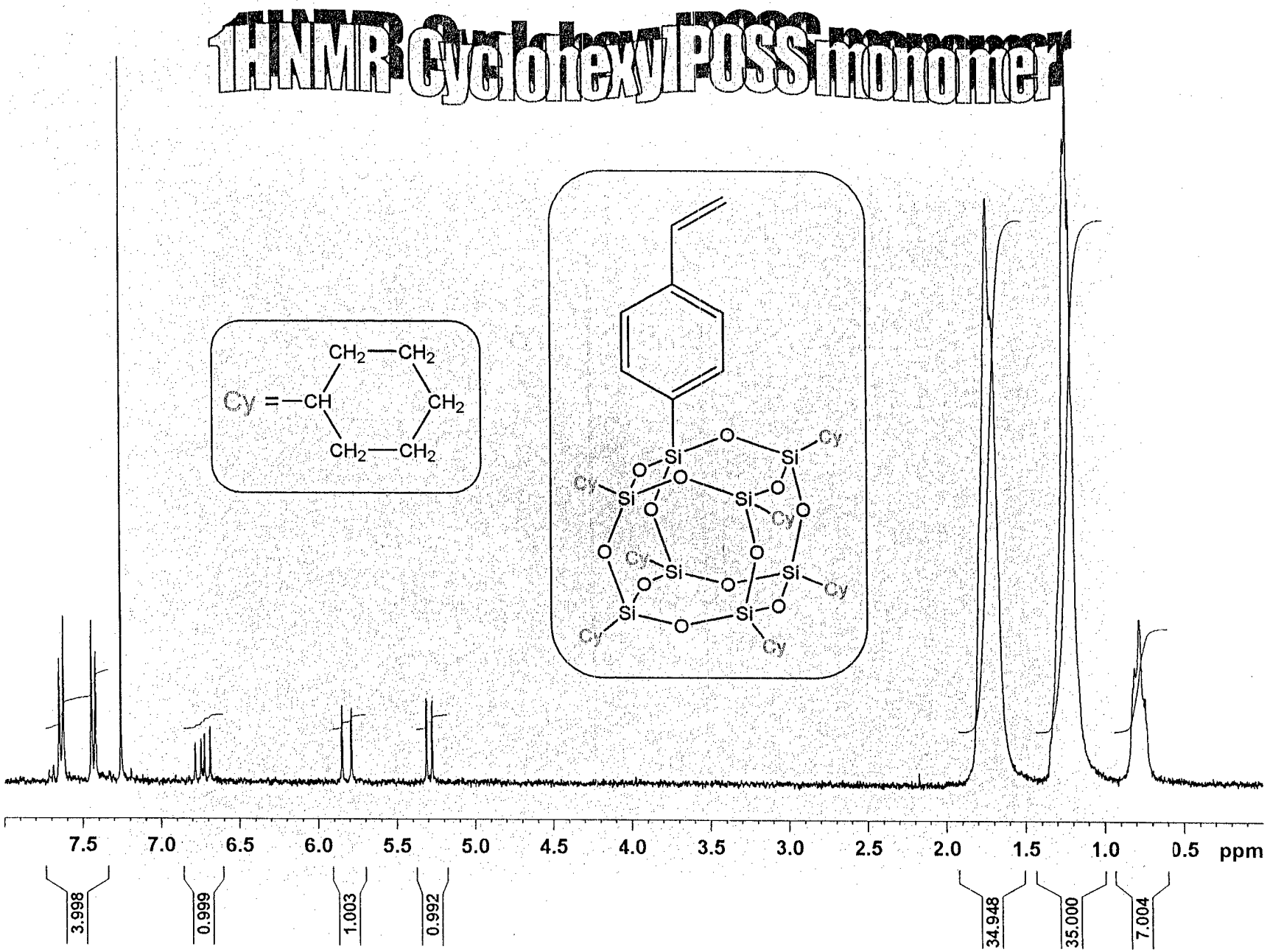
- High-yield syntheses
- Phenyl derivative requires inverse addition
- J. Inorg. Organomet. Polym., Vol 11, 2002, p. 155

POSS Styrene Copolymer Synthesis



- Solution polymerization in toluene or bulk polymerization possible
- Polymerization is limited by solubility of the POSS-macromer
- Isobutyl-POSS is the most soluble, Phenyl-POSS the least soluble
- Macromolecules Vol. 29, 1996 p. 7302

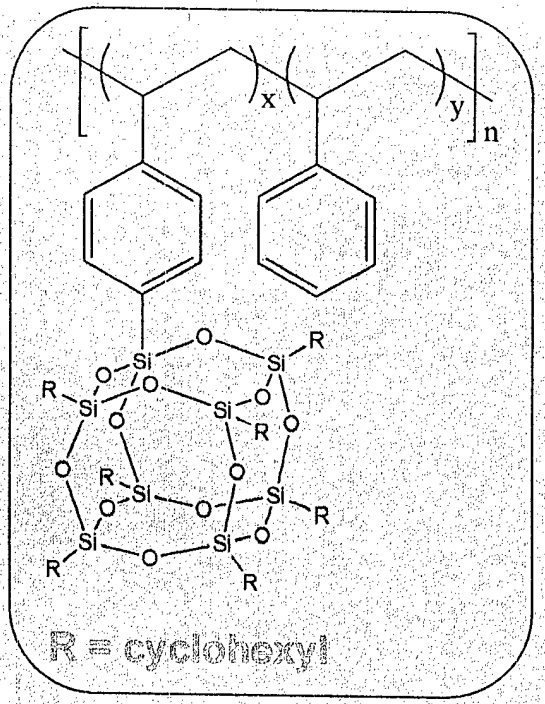
1HNMR Cyclohexyl POSS monomer



1HNMR 50wt%CyPOSS-PS copolymer

IR = Aromatic Integral / Aliphatic Integral

Mole fraction POSS-styrene = (5-3*IR) / (63*IR+1)



No monomer present.

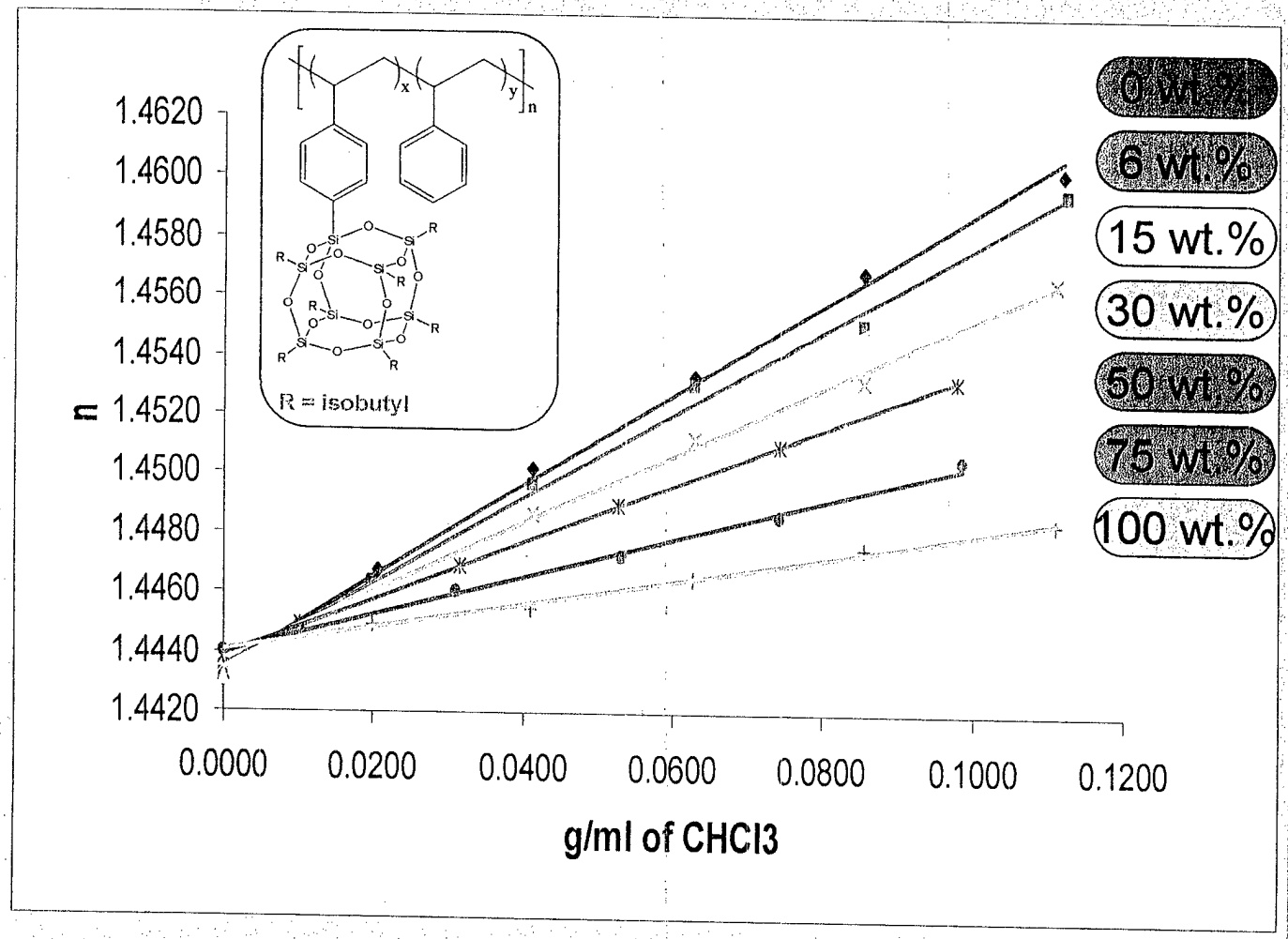
The Specific Refractive Index Increment and POSS Polymer

- The Specific Refractive Index Increment, $dn/dc = (n-n_o)/c$, is the change in RI with change in concentration.
- It is a constant value for a dilute polymer in solution at constant temperature, pressure and wavelength.
- It is useful for determining the Mw of a polymer by light scattering (GPC).
- For copolymers composed of two monomers, the dn/dc is an additive function of the individual weight fractions.

WHY FIND THE dn/dc VALUE?

- To accurately determine the weight average molecular weights of various POSS-polymers.
- To generically parameterize each POSS type (R = cyclohexyl, isobutyl, phenyl etc.) in order to predict POSS-polymer dn/dc values.
- To provide a quick and accurate method to determine POSS % incorporation in any polymer system.

RI vs. Concentration of iBuPOSS-PS copolymer



Slope = dn/dc

Y= 0.1537x+1.4434
R^2 = 0.9966

Y= **0.1428**x+1.4435
R^2 = 0.9958

Y= **0.1327**x+1.4436
R^2 = 0.9929

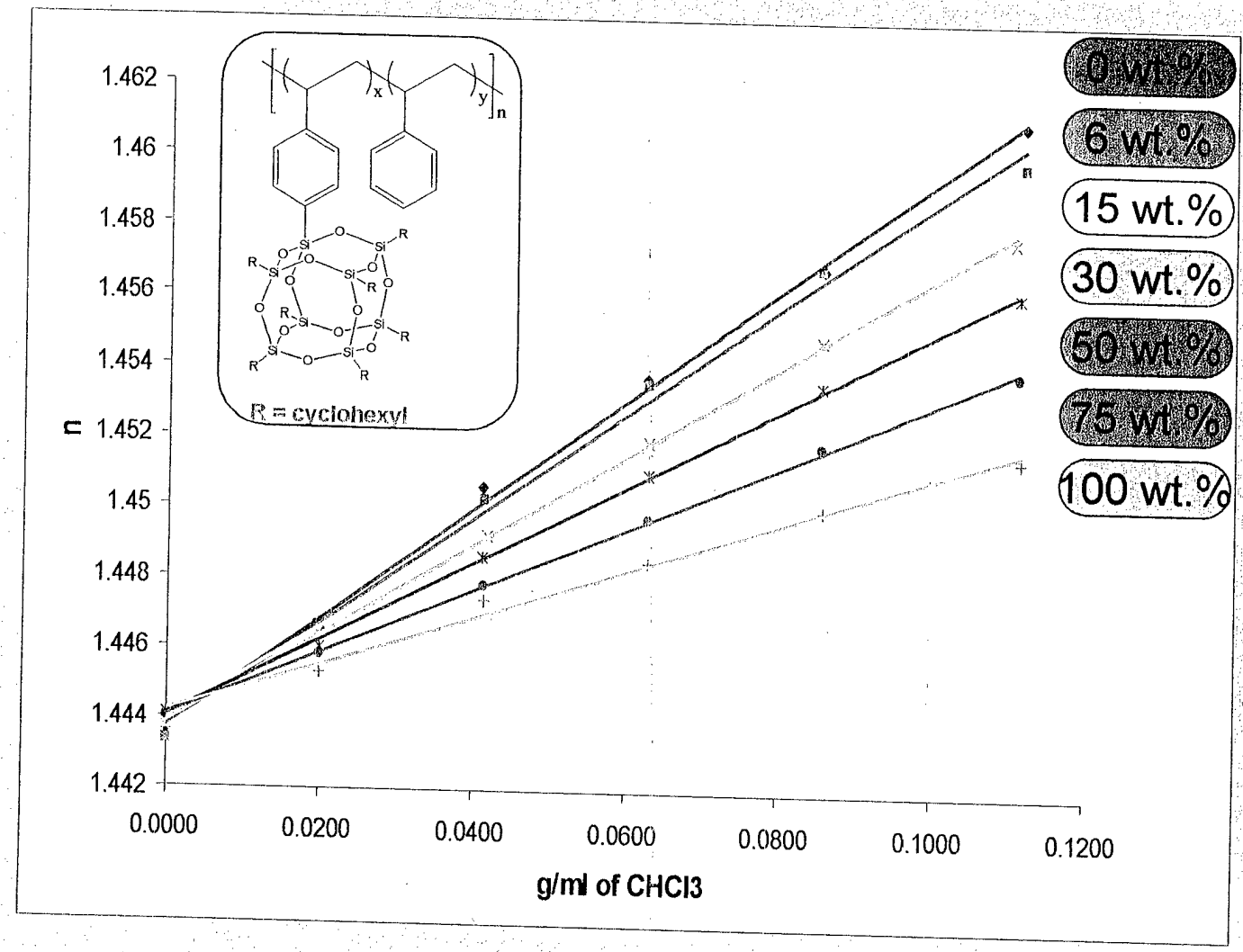
Y= **0.1159**x+1.4437
R^2 = 0.9976

Y= **0.0954**x+1.4439
R^2 = 0.9999

Y= **0.0636**x+1.444
R^2 = 0.9962

Y= **0.0402**x+1.444
R^2 = 0.9976

RI vs. Concentration of CyPOSS-PS copolymer



Slope = dn/dc

Y= 0.1458x+1.4437
R^2 = 0.9976

Y= 0.1488x+1.4437
R^2 = 0.9949

Y=0.1352x+1.4439
R^2 = 0.9985

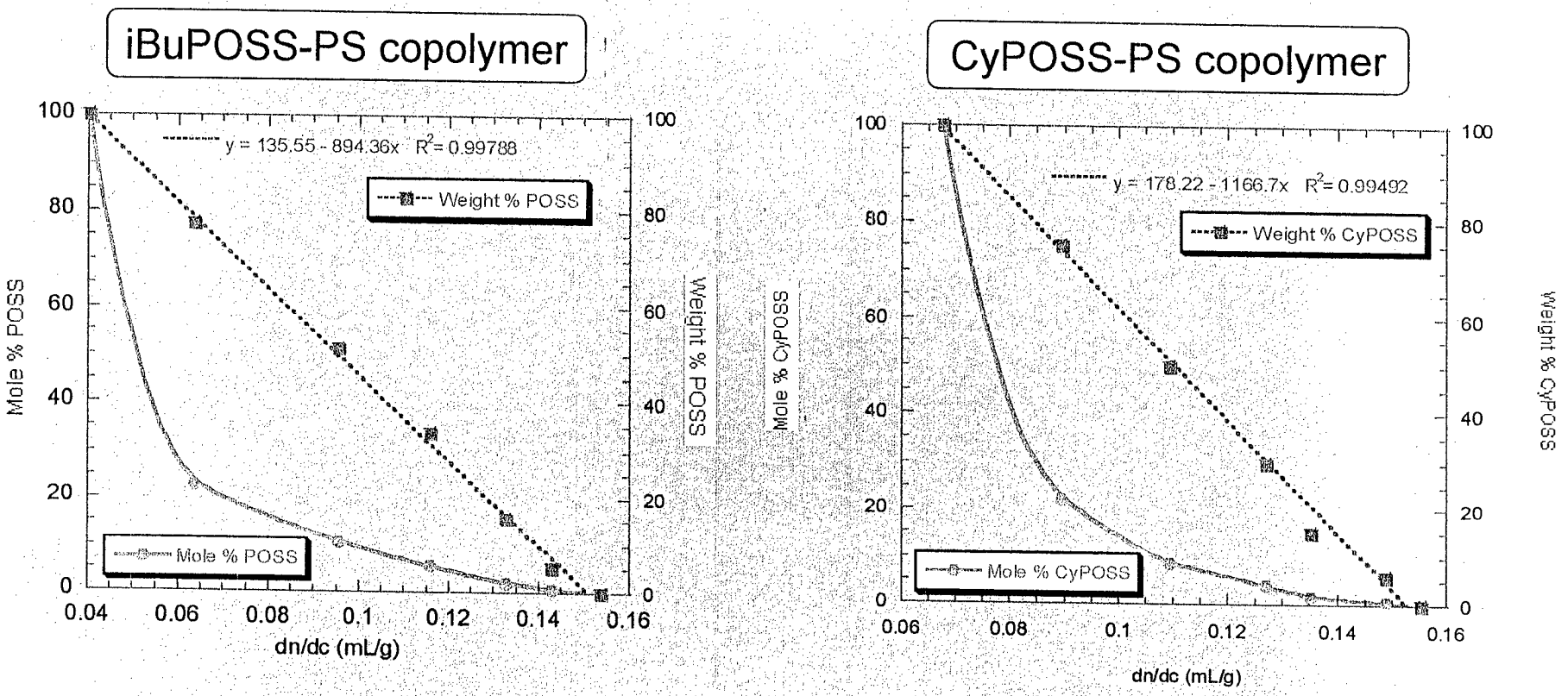
Y=0.1270x+1.4438
R^2 = 0.9995

Y= 0.1092x+1.444
R^2 = 0.9991

Y= 0.0894x+1.444
R^2 = 0.9998

Y= 0.0676x+1.4442
R^2 = 0.9959

dn/dc vs wt% and mole%



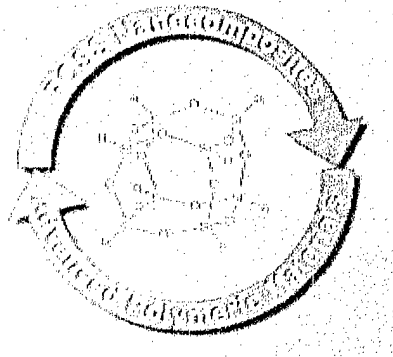
- Clearly, dn/dc is linear with respect to weight % POSS not mole % POSS; changes in refractive index are proportional to the volume occupied by the polymeric components. A typical POSS monomer is about 10X more massive than a typical organic monomer.
- Note that the dn/dc value decreases with increasing POSS incorporation.

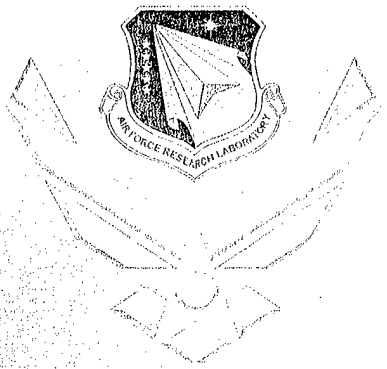
Summary & Future Work

- There is a linear relationship between weight % POSS and the dn/dc of a styrene copolymer.

- To graph a dn/dc / weight % POSS relationship for any new POSS polymer it is reasonable to just measure the dn/dc values of the 0 and 100 % POSS polymer.

- We intend to prove this concept for other glassy (Acrylics) and rubbery (Norbornenes) POSS copolymers.





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